

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
APPLICATION FOR UNITED STATES LETTERS PATENT

Title:

**PHOTORESIST POLYMER AND PHOTORESIST
COMPOSITION CONTAINING THE SAME**

Geun Su Lee	#502-1302 Jugong Green Ville 454 Sanggal-ri, Giheung-eup, Yongin-si Gyeonggi-do 449-905, Korea
Cheol Kyu Bok	7/1, 204-8 Hongeun 3-dong, Seodaemun-gu Seoul 120-100, Korea
Seung Chan Moon	#301, 401 Imgwang Apt., Pungdeokcheon- dong, Suji-eup, Yongin-si Gyeonggi-do 449-846, Korea
Ki Soo Shin	#307-1301 Gisan Apt., Yatap-dong Bundang-gu, Seongnam-si Gyeonggi-do 463-070, Korea
Jae Hyun Kim	625-3 Yodang-ri, Yanggam-myeon Hwaseong-si Gyeonggi-do 445-931, Korea
Jung Woo Kim	625-3 Yodang-ri, Yangganm-myeon Hwaseong-si Gyeonggi-do 445-931, Korea
Sang Hyang Lee	625-3 Yodang-ri, Yanggam-myeon Hwaseong-si Gyeonggi-do 445-931, Korea
Jae Hyun Kang	625-3 Yodang-ri, Yanggam-myeon Hwaseong-si Gyeonggi-do 445-931, Korea

PHOTORESIST POLYMER AND PHOTORESIST
COMPOSITION CONTAINING THE SAME

BACKGROUND

Technical Field

5 Photoresist polymers and photoresist compositions containing the same are disclosed. More specifically, photoresist polymers and photoresist compositions containing the same are disclosed that may improve line edge roughness (hereinafter, referred to as "LER") in a photoresist process using light sources of far ultraviolet regions of 193 nm and 157 nm.

10 **Description of the Related Art**

 In order to be used for ArF and VUV (vacuum ultraviolet) resists, photoresist polymers and photoresist compositions are required to have low light absorbance at wavelengths of 193 nm and 157 nm, excellent etching resistance and adhesive property on the substrate, and to be developed with TMAH solution of 2.38 wt% and
15 2.6 wt%.

 Recently, much research has been conducted on resins having a high transparency at 248 nm and 193 nm wavelengths and dry etching resistance similar to novolac resin.

 Since the thickness of resist materials becomes thinner as circuits of
20 semiconductor devices become more microscopic, improvement of LER of patterns has been promptly required.

 The LER occurs more frequently in ArF resist patterns than in conventional KrF or i-line resist patterns. The conventional KrF or i-line resist materials include acidic alcohol groups while most ArF resist materials do not include acidic alcohol
25 group. As a result, since the ArF resist materials have low affinity to basic

developing solutions, the LER occurs more frequently in the ArF resist materials.

This phenomenon occurs more severely when patterns are formed using chemically amplified photoresist. The LER degrades stability and yield of semiconductor devices for performing a subsequent process.

5

SUMMARY OF THE DISCLOSURE

Photoresist polymers and photoresist compositions containing the same that have high affinity to developing solution are disclosed.

A method for forming photoresist patterns using the disclosed compositions
10 is disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photograph showing a photoresist pattern obtained from Example
8.

15 Fig. 2 is a photograph showing a photoresist pattern obtained from Example
9.

Fig. 3 is a photograph showing a photoresist pattern obtained from Example
10.

20 Fig. 4 is a photograph showing a photoresist pattern obtained from Example
11.

Fig. 5 is a photograph showing a photoresist pattern obtained from Example
12.

Fig. 6 is a photograph showing a photoresist pattern obtained from Example
13.

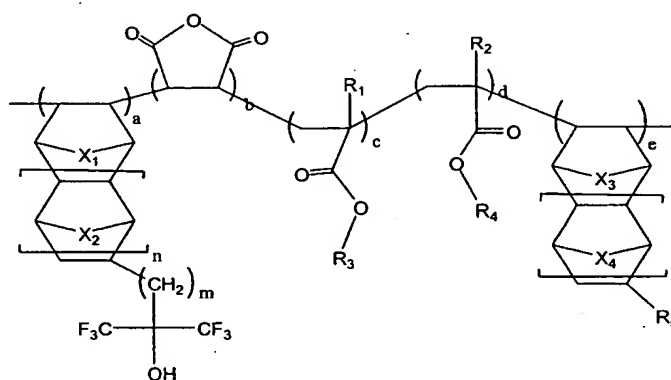
25 Fig. 7 is a photograph showing a photoresist pattern obtained from Example
14.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

Photoresist polymers including acidic alcohol groups and photoresist compositions containing the same are disclosed.

- 5 A photoresist polymer comprises having repeating unit represented by Formula 1:

Formula 1



wherein

- 10 X₁, X₂, X₃ and X₄ individually are selected from the group consisting of CH₂, CH₂CH₂, O and S;

R₁ and R₂ individually are selected from the group consisting of H, CH₃ and CF₃;

- 15 R₃ is selected from the group consisting of acid labile protecting group, C₁-C₂₀ alkyl and C₁-C₂₀ cycloalkyl;

R₄ is selected from the group consisting of C₁-C₂₀ hydroxyalkyl, C₁-C₂₀ hydroxyalkyl having halogen substituent, C₅-C₁₀ alkyl including an ether group, C₅-C₁₀ alkyl including an ester group, C₅-C₁₀ cycloalkyl including an ether group and C₅-C₁₀ cycloalkyl including an ester group;

R₅ is selected from the group consisting of H, C₁-C₂₀ alkyl, C₁-C₂₀ alkyl carboxylate and -O-R₇, wherein R₇ is C₁-C₂₀ cycloalkyl;

m is an integer ranging from 0 to 2;

n is an integer of 0 or 1; and

5 the relative ratio of a : b : c : d : e is in the range 1~20 mol% : 1~20 mol% : 10~60 mol% : 1~40 mol% : 0~30 mol%.

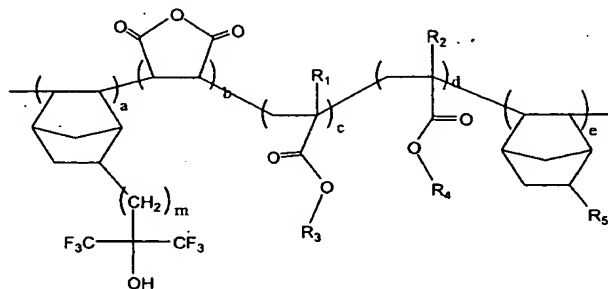
The disclosed polymers including acidic alcohol groups have high affinity to basic developing solutions. In addition, since the disclosed polymers include fluorine atoms, absorbance of conventional hybrid-type photoresist may be improved.

10 The acid labile protecting group which may be left by acid determines solution to an alkaline developing solution. That is, the acid labile protecting group prevents the compound from dissolving in the alkaline developing solution. If the acid labile protecting group is left by acid generated by exposure to light, the photoresist may be dissolved in the developing solution. Some of conventional acid
15 labile protecting groups are disclosed in U.S. Patent No. 5,212,043 (May 18, 1993), WO 97/33198 (Sep 12, 1997), WO 96/37526 (Nov 28, 1996), EP 0 794 458 (Sep 10, 1997), EP 0 789 278 (Aug 13, 1997), U.S. Patent No. 5,750,680 (May 12, 1998), U.S. Patent No. 6,051,678 (Apr 18, 2000), GB 2,345,286 A (July 5, 2000), U.S. Patent No. 6,132,926 (Oct 17, 2000), U.S. Patent No. 6,143,463 (Nov 7, 2000), U.S. Patent No.
20 6,150,069 (Nov 21, 2000), U.S. Patent No. 6,180,316 B1 (Jan 30, 2001), U.S. Patent No. 6,225,020 B1 (May 1, 2001), U.S. Patent No. 6,235,448 B1 (May 22, 2001) and U.S. Patent No. 6,235,447 B1 (May 22, 2001). Preferably, the acid labile protecting group is selected from the group consisting of t-butyl, tetrahydropyran-2-yl, 2-methyl tetrahydropyran-2-yl, tetrahydrofuran-2-yl, 2-methyl tetrahydrofuran-2-yl, 1-methoxypropyl, 1-methoxy-1-methyl ethyl, 1-ethoxypropyl, 1-ethoxy-1-methyl ethyl,
25

1-methoxyethyl, 1-ethoxyethyl, t-butoxyethyl, and 1-isobutoxyethyl and 2-acetylment-1-yl.

Preferably, the polymer comprises repeating unit of Formula 1a:

Formula 1a



5

wherein

R_1 and R_2 individually are selected from the group consisting of H, CH_3 and CF_3 ;

R_3 is selected from the group consisting of acid labile protecting group, C_1 - C_{20} alkyl and C_1 - C_{20} cycloalkyl;

R_4 is selected from the group consisting of C_1 - C_{20} hydroxyalkyl, C_1 - C_{20} hydroxyalkyl having halogen substituent, C_5 - C_{10} alkyl including an ether group, C_5 - C_{10} alkyl including an ester group, C_5 - C_{10} cycloalkyl including an ether group and C_5 - C_{10} cycloalkyl including an ester group;

R_5 is selected from the group consisting of H, C_1 - C_{20} alkyl, C_1 - C_{20} alkyl carboxylate and $-O-R_7$, wherein R_7 is C_1 - C_{20} cycloalkyl;

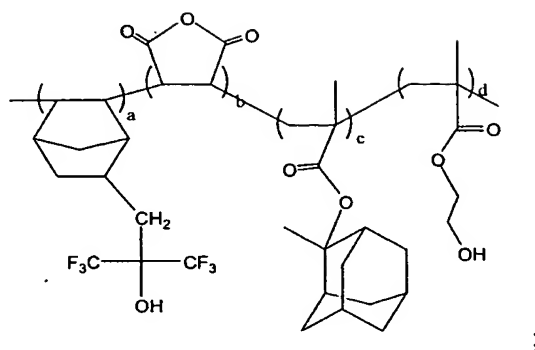
m is an integer ranging from 0 to 2;

n is an integer of 0 or 1; and

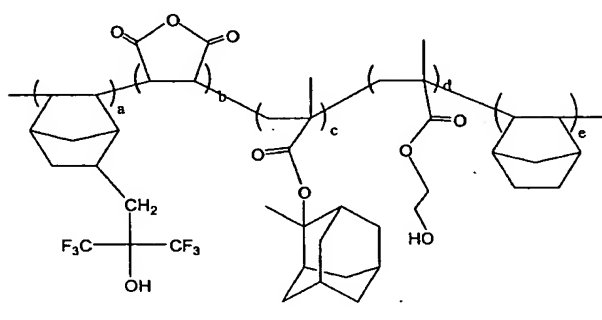
the relative ratio of $a : b : c : d : e$ is in the range 1~20 mol% : 1~20 mol% : 10~60 mol% : 1~40 mol% : 0~30 mol%.

More preferably, the polymer having repeating unit of Formula 1a is selected from the group consisting of Formulas 1b to 1h;

Formula 1b

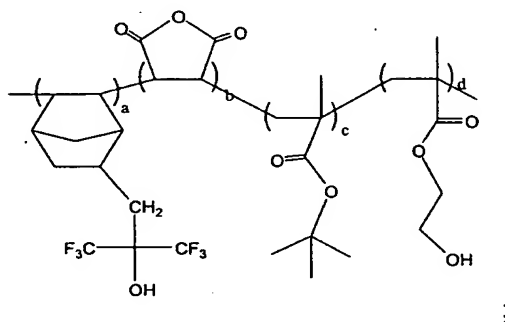


Formula 1c

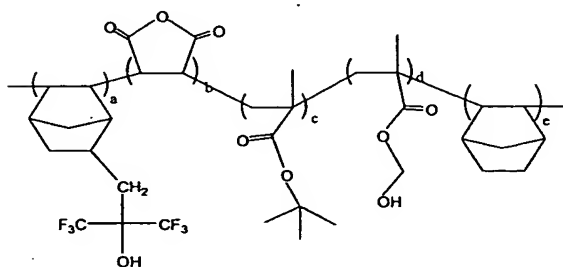


5

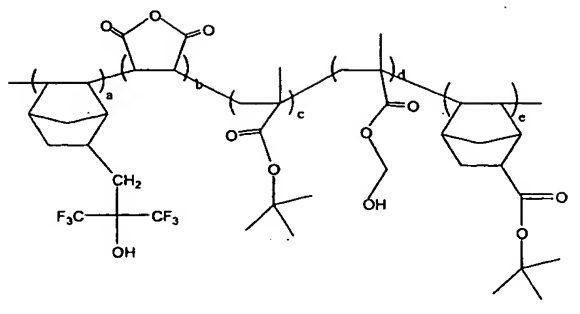
Formula 1d



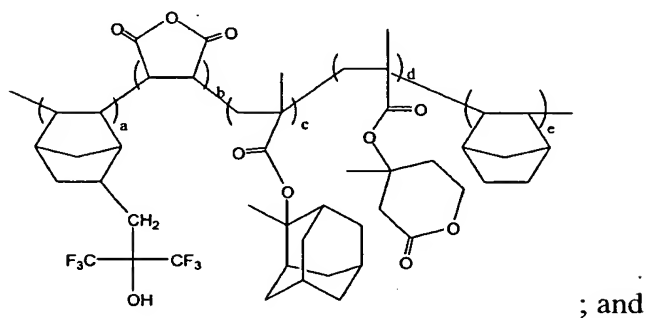
Formula 1e



Formula 1f



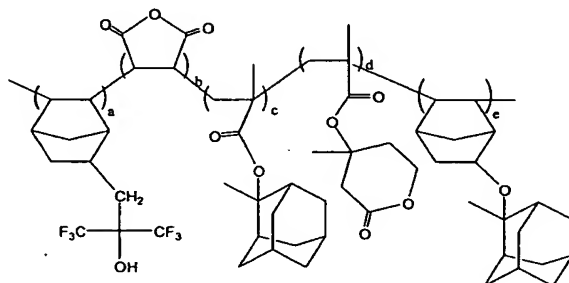
Formula 1g



; and

5

Formula 1h



wherein

the relative ratio of a : b : c : d is in the range 1~20 mol% : 1~20 mol% :

10~60 mol% : 1~40 mol% ; and

10

the relative ratio of a : b : c : d : e is in the range 1~20 mol% : 1~20 mol% :

10~60 mol% : 1~40 mol% : 0~30 mol%.

A method for forming a photoresist polymer comprises:

(a) dissolving maleic anhydride, a compound of Formula 2, a compound of

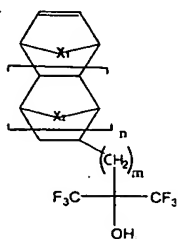
Formula 3, a compound of Formula 4 and optionally a compound of Formula 5 in a polymerization solvent;

(b) adding a polymerization initiator in the resulting solution of the step (a);

and

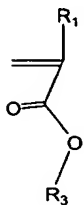
- 5 (c) reacting the resulting solution of the step (b) under a nitrogen or argon atmosphere to obtain a polymer having repeating unit of Formula 1 at a temperature ranging from 60 to 70°C for 4 to 24 hours.

Formula 2

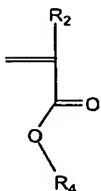


10

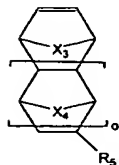
Formula 3



Formula 4



Formula 5



15

wherein

X₁, X₂, X₃ and X₄ individually are selected from the group consisting of CH₂, CH₂CH₂, O and S;

R₁ and R₂ individually are selected from the group consisting of H, CH₃ and CF₃;

5 R₃ is selected from the group consisting of acid labile protecting group, C₁-C₂₀ alkyl and C₁-C₂₀ cycloalkyl;

R₄ is selected from the group consisting of C₁-C₂₀ hydroxyalkyl, C₁-C₂₀ hydroxyalkyl having halogen substituent, C₅-C₁₀ alkyl including an ether, C₅-C₁₀ alkyl including an ester group, C₅-C₁₀ cycloalkyl including an ether and C₅-C₁₀ cycloalkyl
10 including an ester group;

R₅ is selected from the group consisting of H, C₁-C₂₀ alkyl, C₁-C₂₀ alkyl carboxylate and -O-R₇, wherein R₇ is C₁-C₂₀ cycloalkyl;

m is an integer ranging from 0 to 2; and

n is an integer of 0 or 1.

15 The polymerization reaction which is radical polymerization is performed as types of bulk polymerization or solution polymerization. As disclosed in WO 96/37526 (Nov 28, 1996), the polymerization may be performed using metal catalyst.

Preferably, the polymerization solvent of the step (a) is selected from the group consisting of cyclohexanone, cyclopentanone, tetrahydrofuran,
20 dimethylformamide, dimethylsulfoxide, dioxane, methylethylketone, benzene, toluene, xylene and mixtures thereof.

Additionally, the polymerization initiator of the step (b) is preferably selected from the group consisting of benzoyl peroxide, 2,2'-azobisisobutyronitrile (AIBN), acetylperoxide, laurylperoxide, t-butylperacetate, t-butylhydroperoxide and di-t-
25 butylperoxide.

The polymer obtained from the step (c) is preferably crystallized and purified using single or mixture solution selected from the group consisting of dimethylether, petroleum ether, methanol, ethanol, lower alcohol including iso-propanol, and water.

In addition, a photoresist composition is disclosed that comprises the
5 photoresist polymer of Formula 1, a photoacid generator and an organic solvent.

Any of conventional photoacid generators, which are able to generate acids when they are exposed to light, can be used. Some of conventional photoacid generators are disclosed in U.S. Patent No. 5,212,043 (May 18, 1993), WO 97/33198 (Sep 12, 1997), WO 96/37526 (Nov 28, 1996), EP 0 794 458 (Sep 10, 1997), EP 0
10 789 278 (Aug 13, 1997), U.S. Patent No. 5,750,680 (May 12, 1998), U.S. Patent No. 6,051,678 (Apr 18, 2000), GB 2,345,286 A (Jul 5, 2000), U.S. Patent No. 6,132,926 (Oct 17, 2000), U.S. Patent No. 6,143,463 (Nov 7, 2000), U.S. Patent No. 6,150,069 (Nov 21, 2000), U.S. Patent No. 6,180,316 B1 (Jan 30, 2001), U.S. Patent No. 6,225,020 B1 (May 1, 2001), U.S. Patent No. 6,235,448 B1 (May 22, 2001) and U.S.
15 Patent No. 6,235,447 B1 (May 22, 2001). Sulfide type or onium type compounds are primarily used for the photoacid generator.

More preferably, the photoacid generator is selected from the group consisting of phthalimidotrifluoromethane sulfonate, dinitrobenzyl-tosylate, n-decyl disulfone and naphthylimido trifluoromethane sulfonate having low absorbance at
20 157 nm and 193 nm. Also, the photoacid generator may be further selected from the group consisting of diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenylsulfonium triflate, diphenyl p-toluenyl-sulfonium triflate, diphenyl p-isobutylphenyl-sulfonium triflate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoro-
25 antimonate, triphenyl-sulfonium triflate, and dibutyl-naphthylsulfonium triflate.

The photoacid generator is preferably present in an amount ranging from 0.05 to 10 wt% based upon the amount of the photoresist polymer present. If the photoresist generator is present in the amount of less than 0.05 wt%, it lowers photosensitivity of the photoresist composition to light. If the photoacid generator is present in the amount of more than 10 wt%, it results in a poor pattern formation due to its high absorption of far ultraviolet rays.

Any of the organic solvents can be used. Some of conventional organic solvents are disclosed in U.S. Patent 5,212,043 (May 18, 1993), WO 97/33198 (Sep 12, 1997), WO 96/37526 (Nov 28, 1996), EP 0 794 458 (Sep 10, 1997), EP 0 789 278 (Aug 13, 1997), U.S. Patent No. 5,750,680 (May 12, 1998), U.S. Patent No. 6,051,678 (Apr 18, 2000), GB 2,345,286 A (Jul 5, 2000), U.S. Patent No. 6,132,926 (Oct 17, 2000), U.S. Patent No. 6,143,463 (Nov 7, 2000), U.S. Patent No. 6,150,069 (Nov 21, 2000), U.S. Patent No. 6,180,316 B1 (Jan 30, 2001), U.S. Patent No. 6,225,020 B1 (May 1, 2001), U.S. Patent No. 6,235,448 B1 (May 22, 2001) and U.S. Patent No. 6,235,447 B1 (May 22, 2001). Preferably, the organic solvent is selected from the group consisting of diethylene glycol diethyl ether, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, propylene glycol methyl ether acetate, cyclohexanone, 2-heptanone, and ethyl lactate.

The organic solvent is present in an amount ranging from 500 to 2000 wt% to the photoresist polymer in order to obtain a desired thickness of the photoresist film. For example, the thickness of the photoresist film is about 0.25 μm when the organic solvent is present in the amount of about 1000 wt% based upon the amount of the photoresist polymer present.

A method for forming a photoresist pattern comprises:

(a) coating the photoresist composition disclosed above on a wafer to form a photoresist film;

- (b) exposing the photoresist film to light;
- (c) baking the exposed photoresist film; and
- (d) developing the photoresist film to obtain a photoresist pattern.

The above method may further comprise performing a bake process before
5 exposure of the step (b). Here, the bake process is performed at a temperature ranging from 70 to 200°C.

The exposure process is performed using the light selected from the group consisting of KrF, ArF, EUV (Extreme Ultra Violet), VUV (Vacuum Ultra Violet), E-beam, X-ray and ion beam with exposure energy ranging from 0.1 to 100 mJ/cm².

10 The development of step (d) is preferably performed using an alkaline developing solution such as TMAH aqueous solution in an amount ranging from 0.01 to 5 wt%.

A semiconductor device manufactured according to the method described above is also disclosed.

15 The disclosed photoresist polymers and photoresist compositions containing the same will be described in greater detail by referring to examples below, which are not intended to be limiting.

I. Preparation of photoresist polymers

Example 1--Synthesis of Compound of Formula 1b

20 To tetrahydrofuran (60mL) were added 3-(5-bicyclo[2.2.1]-heptene-2-yl)-1,1,1-(trifluoromethyl)propane-2-ol (0.015 M) (CAS# 196314-61-1), maleic anhydride (0.015 M), 2-methyl-2-adamantyl methacrylate (0.05 M), 2-hydroxyethyl methacrylate (0.02 M) (CAS# 868-77-9) and AIBN (0.2 g). The resulting mixture was reacted at 65 °C for 24 hours. After reaction the resulting mixture was distilled under reduced
25 pressure. Then, polymers were precipitated in diethylether/hexane and filtered, thereby obtaining the polymer of Formula 1b (yield: 52%).

Example 2--Synthesis of Compound of Formula 1c

To tetrahydrofuran (60 mL) were added 3-(5-bicyclo[2.2.1]-heptene-2-yl)-1,1,1-(trifluoromethyl)propane-2-ol (0.01 M), maleic anhydride (0.02 M), 2-methyl-2-adamantyl methacrylate (0.05 M), 2-hydroxyethyl methacrylate (0.01 M),
5 norbornylene (CAS# 498-66-8) and AIBN (0.2 g). The resulting mixture was reacted at 65 °C for 24 hours. After reaction the resulting mixture was distilled under reduced pressure. Then, polymers were precipitated in diethylether/hexane and filtered, thereby obtaining the polymer of Formula 1c (yield: 56%).

Example 3--Synthesis of Compound of Formula 1d

10 To tetrahydrofuran (60 mL) were added 3-(5-bicyclo[2.2.1]-heptene-2-yl)-1,1,1-(trifluoromethyl)propane-2-ol (0.015 M), maleic anhydride (0.015M), t-buthyl methacrylate (0.05 M) (CAS# 585-07-9), 2-hydroxyethyl methacrylate (0.02 M) and AIBN (0.2 g). The resulting mixture was reacted at 65 °C for 24 hours. After
reaction the resulting mixture was distilled under reduced pressure. Then, polymers
15 were precipitated in water/ethanol and filtered, thereby obtaining the polymer of Formula 1d (yield: 52%).

Example 4--Synthesis of Compound of Formula 1e

To tetrahydrofuran (60mL) were added 3-(5-bicyclo[2.2.1]-heptene-2-yl)-1,1,1-(trifluoromethyl)propane-2-ol (0.015 M), maleic anhydride (0.025 M), t-buthyl
20 methacrylate (0.04 M), 2-hydroxymethyl methacrylate (0.01 M), norbornylene (0.01 M) and AIBN (0.2 g). The resulting mixture was reacted at 65 °C for 24 hours. After reaction the resulting mixture was distilled under reduced pressure. Then, polymers were precipitated in water/ethanol and filtered, thereby obtaining the polymer of Formula 1e (yield: 52%).

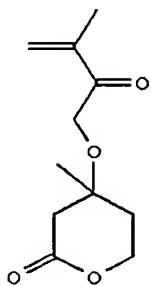
Example 5--Synthesis of Compound of Formula 1f

To tetrahydrofuran (60mL) were added 3-(5-bicyclo[2.2.1]-heptene-2-yl)-1,1,1-(trifluoromethyl)propane-2-ol (0.015 M), maleic anhydride (0.025 M), t-buthyl methacrylate (0.03 M), 2-hydroxymethyl methacrylate (0.02 M), t-buthyl-5-norbornene-2-carboxylate (0.01 M) (CAS# 154970-45-3) and AIBN (0.2 g). The resulting mixture was reacted at 65 °C for 24 hours. After reaction the resulting mixture was distilled under reduced pressure. Then, polymers were precipitated in water/ethanol and filtered, thereby obtaining the polymer of Formula 1f (yield: 52%).

Example 6--Synthesis of Compound of Formula 1g

To tetrahydrofuran (60mL) were added 3-(5-bicyclo[2.2.1]-heptene-2-yl)-1,1,1-(trifluoromethyl)propane-2-ol (0.015 M), maleic anhydride (0.025 M), 2-methyl-2-adamantyl methacrylate (0.04 M), the compound of Formula 6 (0.01 M), norbornylene (0.01 M) and AIBN (0.2 g). The resulting mixture was reacted at 65 °C for 24 hours. After reaction the resulting mixture was distilled under reduced pressure. Then, polymers were precipitated in water/ethanol and filtered, thereby obtaining the polymer of Formula 1 g (yield : 58%).

Formula 6



Example 7--Synthesis of Compound of Formula 1h

To tetrahydrofuran (60 mL) were added 3-(5-bicyclo[2.2.1]-heptene-2-yl)-1,1,1-(trifluoromethyl)propane-2-ol (0.015 M), maleic anhydride (0.025 M), 2-methyl-2-adamantyl methacrylate (0.04M), the compound of Formula 6, 2-methyl-2-

adamanthyl-5-norbornene-2-carboxylate (0.01 M) and AIBN (0.2 g). The resulting mixture was reacted at 65 °C for 24 hours. After reaction the resulting mixture was distilled under reduced pressure. Then, polymers were precipitated in water/ethanol and filtered, thereby obtaining the polymer of Formula 1h (yield : 49%).

5 **II. Preparation of photoresist compositions and Formation of Patterns**

Example 8

To propyleneglycolmethyl ether acetate (PGMEA) (20 g) were added the polymer (2 g) obtained from Example 1, phthalimidotrifluoromethane sulfonate
10 (0.024 g) and triphenylsulfonium triflate (0.06 g) which are photoacid generators. The resulting mixture was filtered with a 0.20 µm filter, thereby obtaining a photoresist composition.

The photoresist composition was spin-coated on a silicon wafer to form a photoresist film, and soft-baked at 130 °C for 90 seconds. After baking, the
15 photoresist was exposed to light using an ArF laser exposer, and then post-baked at 130 °C for 90 seconds. The baked wafer was developed in 2.38 wt% TMAH aqueous solution for 40 seconds to obtain 0.08 µm of L/S pattern (see Fig. 1).

Example 9

The procedure of Example 8 was repeated using the polymer (2 g) of
20 Example 2 instead of the polymer of Example 1 to obtain the pattern of 0.08 µm of L/S pattern (see Fig. 2).

Example 10

The procedure of Example 8 was repeated using the polymer (2 g) of
Example 3 instead of the polymer of Example 1 to obtain the pattern of 0.08 µm of
25 L/S pattern (see Fig. 3).

Example 11

The procedure of Example 8 was repeated using the polymer (2 g) of Example 4 instead of the polymer of Example 1 to obtain the pattern of 0.08 μm of L/S pattern (see Fig. 4).

5

Example 12

The procedure of Example 8 was repeated using the polymer (2 g) of Example 5 instead of the polymer of Example 1 to obtain the pattern of 0.08 μm of L/S pattern (see Fig. 5).

Example 13

10

The procedure of Example 8 was repeated using the polymer (2 g) of Example 6 instead of the polymer of Example 1 to obtain the pattern of 0.08 μm of L/S pattern (see Fig. 6).

Example 14

15 The procedure of Example 8 was repeated using the polymer (2 g) of Example 7 instead of the polymer of Example 1 to obtain the pattern of 0.08 μm of L/S pattern (see Fig. 7).

As discussed earlier, patterns having the improved LER can be obtained because the disclosed photoresist compositions including acidic alcohol groups have high affinity to basic developing solutions. Additionally, ultra microscopic patterns of 4 G, 16 G DRAMs as well as of less than 1 G DRAM can be obtained because the disclosed photoresist compositions containing polymers including fluorine have low absorbance at 193 nm and 157 nm.

20